PATENT SPECIFICATION (11) 1 268 264

(54) SULFONATED ELASTOMERS

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to novel elastomers containing sulfonic acid groups or sulfonic acid salt moieties and to a process for preparing said elastomers. The term "elastomer" is employed in the specification and claims in its normal meaning of a polymer having rubber-like characteristics such as elasticity.

Polymers generally fall into two broad classes, thermoplastic and thermosetting resins. The thermoplastic resins may be readily worked by heating the polymer up to its softening point or melting point. They may then be processed by such deformation methods as vacuum forming, extrusion of a melt, compression molding, etc.

The thermoset resins can ordinarily not be reworked once they have hardened. In general, thermoset resins owe their unique properties to covalent crosslinks between polymer molecules. The crosslinks may be introduced, for example, by interaction of various monomers or other additives with or without heating.

Uncured elastomers such as natural rubber and butyl rubber are thermoplastic. They may, however, be crosslinked by vulcanization by the use of sulfur and accelerators which react with the carbon of the unsaturated bonds in the polymer molecules to form in effect a thermoset product which can no longer be fabricated or worked, except e.g. by machining. The vulcanized polymers have found wide utility because of the significant improvement in physical properties obtained by the crosslinking. Natural rubber, for example, may be crosslinked by vulcanization by the use of sulfur which reacts with the carbon of the unsaturated bonds in the polymer molecule to form a bridge between two molecules so that one polymer molecule is covalently bonded to the second molecule. If sufficient crosslinks of this type occur, all molecules are joined in a single giant molecule. Once crosslinked, the polymer is intractable and can no longer be fabricated except possibly by machining. It has, however, significantly improved physical properties. Thus, by vulcanizing rubber, elasticity, impact resistance, flexibility, thermostability and many other properties are either introduced or improved.

A third class of polymers, known as ionic polymers, has recently been developed which, although they are crosslinked, have a melt or softening point or softening range and may even be dissolved in various solvents. At normal use temperatures, these ionic polymers behave similar to crosslinked polymers. At elevated temperatures, however, they are readily deformed and worked in the same manner as thermoplastic resins. These ionic polymers (ionomers) owe their unique properties to the fact that crosslinking has been accomplished by ionic rather than covalent bonding between molecules of the polymer. Typical of these ionic polymers are copolymers of ethylene and ethylenically unsaturated mono- or dicarboxylic acids which have been neutralized by metal salts (see, for example, British patent 1,011,981 and U.S. patent 3,264,272).

Sulfonic acid ionmers have been prepared by copolymerization of a styrene sulfonic acid salt and other monomers to form plastic polymers containing ionic cross-links, see, for example, U.S. patent 3,322,734.

Methods of sulfonating polymers are well known to the art. For example, aromatic containing polymers are sulfonated by a method described in U.S. patent 3,072,618, wherein a complex of a lower alkyl phosphate and SO_3 is used as the sulfonating agent. These sulfonated aromatic polymers have generally been sulfonated to a sufficient extent to be water-soluble in their acid form. Other aromatic containing resins have been sulfonated, converted to their alkali metal salts and used as ion exchange resins. Water-soluble polymers have been prepared by reacting aromatic rings in styrene-butyl rubber graft polymers with SO_3 to form a viscous sulfonation product, see, for example, U.S.S.R. patent No. 211,079.

It has surprisingly been found that the physical properties of aromatic containing polymers may be improved by sulfonating the polymer to contain 0.2 to 21 mole % sulfonic acid groups. The tensile strength, Young modulus, and high temperature melt strength may be further improved by converting at least a portion of the sulfonic acid moieties to their corresponding amine or metal salts.

According to the present invention there is provided a sulfonated elastomer containing monocyclic aromatic groups and 0.2 to 21 mole % sulfonic acid groups as herein defined.

In particular the sulfonated elastomers of this invention can be prepared by (a) dissolving the unsulfonated form of the elastomer in a solvent which is also a solvent for the said complex of (b), and (b) reacting the elastomer at a temperature between —100° and 100° C with a sulfonating agent comprising (for example one to four moles of) sulfur trioxide and (for example one mole of) a complexing agent, selected from the Lewis bases containing oxygen, phosphorus or nitrogen, to introduce 0.2 to 21 mole % sulfonic acid groups into the elastomer. The sulfonated elastomer so formed can be ionically crosslinked by neutralization with metal salts, amines or amine derivatives (as hereinafter specified whereby at least 1% of the sulfonic acid groups are in the corresponding salt form.

When employed in connection with the products and process of this invention, the term " aromatic " in " aromatic nuclei ", " aromatic groups ", " aromatic units ", means monocyclic aromatic.

The expression " butyl rubber " as employed in the specification and claims means copolymers made from a polymerization reaction mixture having therein from 70 to 99.8% by weight of a C_4 to C_7 isoolefin, e.g. isobutylene, and 30 to 0.2% by weight of a C_4 to C_{14} conjugated multiolefin, e.g. isoprene. The resulting copolymer contains 85 to 99.8% by weight of combined isoolefin and 0.2 to 15% of combined multiolefin.

Butyl rubber generally has a Staudinger molecular weight of about 20,000 to about 500,000, preferably about 25,000 to about 400,000, especially about 100,000 to about 400,000; and a Wijs Iodine No. of about 0.5 to 50, preferably 1 to 15. The preparation of butyl rubber is described in U.S. patent 2,356,128.

For the purposes of this invention, it is preferred that the butyl rubber has incorporated therein from about 0.5 to 6% of combined multiolefin, more preferably 0.5 to 3%, e.g. 2%.
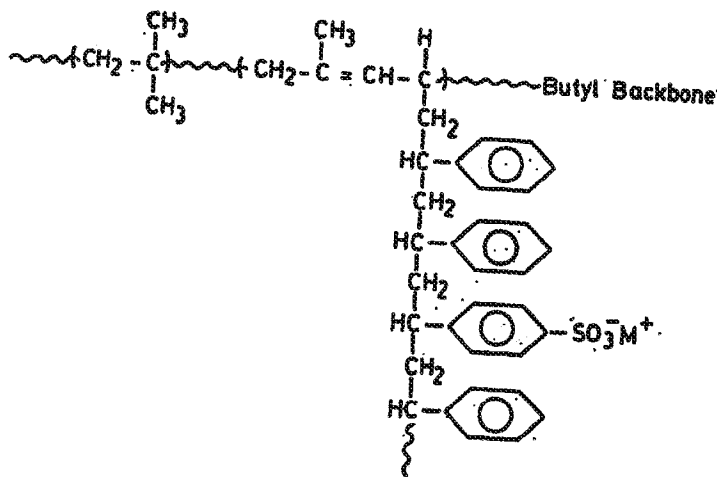
The first step in the preparation of sulfonated butyl rubber elastomers and corresponding ionomers of this invention is the grafting of styrene to the butyl rubber backbone. The grafting is accomplished by halogenation of the butyl rubber and subsequently reacting cationically polymerizable monomers (i.e. styrene) in the presence of an aluminum alkyl or haloaluminum alkyl catalyst. The graft polymer is then reacted with a complex of sulfur trioxide with a Lewis base in order to sulfonate the aromatic ring. The elastomer can then be converted to an ionomer by neutralizing the sulfonic acid moiety.

Halogenated butyl rubber is commercially available and may be prepared by halogenating butyl rubber in a solution containing between 1 to 60% by weight of butyl rubber in a substantially inert C_5—C_8 hydrocarbon solvent such as pentane, hexane, heptane, etc., and contacting this butyl rubber cement with a halogen gas for a period of about 25 minutes whereby halogenated butyl rubber and a hydrogen halide are formed, the copolymer containing up to one halogen atom per double bond in the copolymer. The preparation of halogenated butyl rubbers is old in the art, see e.g. U.S. Patent 3,099,644. This invention is not intended to be limited in any way by the manner in which butyl rubber is halogenated and both chlorinated and brominated butyl rubber are suitable for use in this invention.

Illustrative of commercial halogenated butyl rubber is a chlorinated butyl rubber having about 1.25 wt. % chlorine, 2 mole % unsaturation and a viscosity average molecular weight of about 357,000.
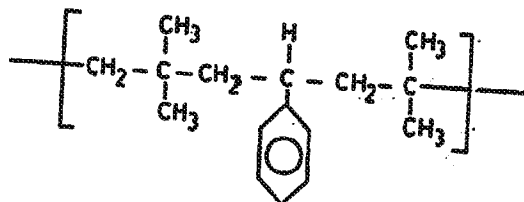
The preparation of butyl rubber-styrene graft polymers from halogenated butyl rubber is disclosed, Belgian patent 701,850.

The structure of the ionomer former from a sulfonated butyl rubber-styrene graft polymer is thought to be:

$$\sim\!\!\!\leftarrow CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \!\!\!\leftarrow\!\!\!\sim\!\!\!\leftarrow CH_2 - \underset{|}{\overset{\overset{CH_3}{|}}{C}} = CH - \underset{\underset{CH_2}{|}}{\overset{\overset{H}{|}}{C}} \!\!\!\leftarrow\!\!\!\sim\!\!\!\sim Butyl\ Backbone$$

where M^+ is a metallic ion of Group I or, less preferably, of Groups II, III, IV, V, VI—B, VII—B and VIII of the Periodic Table (hereinafter identified) of the Elements may also be used.

It will be readily evident that the technique disclosed is applicable to the formation of sulfonate ionomers from any elastomer containing an aromatic nucleus ring in its structure. A particularly suitable elastomer is homogeneous styrene isobutylene copolymer of the general structural unit:

$$\left[-CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - \underset{|}{\overset{\overset{H}{|}}{C}} - CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \right]$$

The term " homogeneous " is used to distinguish this polymer from more conventional styrene-isobutylene copolymers which are in fact predominantly polymer blends of polystyrene and polyisobutylene.

Such homogeneous polymers may be prepared by solution polymerization under steady-state continuous polymerization conditions in a well-mixed tank type reactor. Solvent for the polymerization is either hexane or a hexane rich blend of hexane with methyl chloride. The polymer may contain as little as 0.5 mole % styrene or as much as 90 mole % styrene.

Other elastomers which may be sulfonated by the process of this invention include copolymers of styrene and butadiene, styrene and isoprene, chloroprene and styrene, acrylonitrile and styrene (SAN), styrene and acrylic acid, graft polymers of styrene onto polybutadiene, graft polymers of styrene-acrylonitrile copolymers (SAN) onto polybutadiene (ABS), styrene-isobutylene-isoprene terpolymers, etc.

A typical sulfonation procedure comprises contacting the polymer at about 0 to 100° C. for a period of a few seconds to several hours with a sulfonating complex which is preferably prepared by reacting about 2 to about 4 moles of sulfur trioxide with 1 mole of a phosphorous compound and recovering the sulfonated polymer.

In carrying out the present invention, an alkenyl aromatic-containing polymer is sulfonated with a sulfonating agent comprising a sulfur trioxide donor in combination with a Lewis base complexing agent. In its preferred embodiment, the Lewis base is a lower trialkyl phosphate.

The term "sulfur trioxide donor" as used in the specification and claims means those substances including SO_3, containing sulfur trioxide in a loosely bound form, from which it can readily be liberated. Illustrative of the sulfur trioxide donors of this invention are sulfur trioxide, fuming sulfuric acid ("oleum", 20—80%), chlorosulfonic acid, and fluorosulfonic acid. The term "complexing agent" as used in the specification and claims means the Lewis bases suitable for use in the practice of this invention.

The term "Lewis base" as used herein is used in its usual manner to define materials which donate electron pairs to form covalent bonds. It is intended to include well-known Lewis bases as well as other complexing agents which act as Lewis bases in the sulfonation reaction.

In a preferred embodiment, the base and sulfur trioxide donor are contacted (to form a complex) prior to admixing them with the polymer. However, it is not essential to premix the sulfur trioxide donor with the complexing agent, but rather it is only necessary to have the latter compound present during the sulfonating reaction. For instance, the available sulfur trioxide donor and complexing agent may be admixed simultaneously with the polymer and the complex may be formed in situ in the sulfonating zone.

Because the complexing agent affects the reactivity of the sulfur trioxide donor, the sulfonation temperature need not be maintained below 0° C., but rather it may vary from as low as —100° C, to as high as 100° C. Moreover, the pressure is not a critical condition and may be adjusted to any satisfactory level. For instance, the sulfonation may be carried out from a reduced pressure of, say, 0.5 atmosphere up to a superatmospheric pressure in the area of 10 atmospheres. The most suitable conditions from an economic standpoint are temperatures of 15° to 40° C. and pressures which are approximately atmospheric. The sulfonation time will, of course, vary with the particular conditions selected, the compound being sulfonated, and the complex used. Generally, the reactions are complete within a few seconds to several hours after the reactants are contacted with each other. When sulfonating at approximately room temperature and atmospheric pressure, the contact time should be 5 seconds to 25 or 30 minutes. Since the complexing agent reduces the activity of the sulfur trioxide donor, it is not necessary to limit the sulfonating time as is required in conventional processes.

Illustrative of Lewis bases suitable for use as complexing agents are certain phosphorous compounds. While the phosphorous compound may be either inorganic or organic, it is preferred that the phosphorous compound be an organic compound having the general formula:
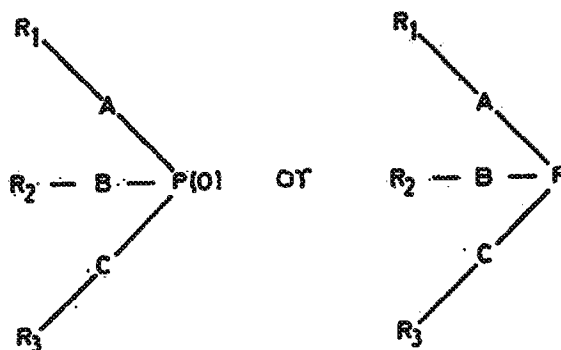
wherein A, B and C are each independently oxygen, or —CH_2—; and R_1, R_2 R_3 are each independently selected from the group consisting of C_1 to C_{25} alkyl, aryl, alkaryl or aralkyl. Various organic phosphites, phosphinites, phosphinates, phosphates, phosphonates, phosphonites and phosphines may be used as the complexing agent.

Illustrative of phosphorus containing inorganic complexing agents are phosphoric acid, phosphorous acid, pyrophosphoric acid, metaphosphoric acid, phosphonic acid and phosphinic acid. In addition to the acids, their mono-, di- and tri-substituted derivatives may also be employed. However, the preferred phosphorous compounds are the trialkyl phosphates and phosphites.

Illustrative of other organic phosphorous compounds suitable for use as complexing agents are: triethyl phosphate, trimethyl phosphate, tripropyl phosphate, tri-butyl phosphate, triethyl phosphite, etc.

Other organic compounds suitable for use as complexing agents include the organic pyrophosphates. These compounds have the general formula:

$$R_4R_5R_6R_7P_2O_7$$

wherein R_4, R_5, R_6 and R_7 are each independently H, C_1 to C_{12} alkyl, aryl, aralkyl or alkaryl, with the proviso that at least two of the groups are not H. The groups may be halogen-substituted. Phenyl groups may be either halogen or nitro-substituted. As used in the specification the term "substituted derivatives thereof" when used in reference to these R_4 to R_7 groups means nitro or halogen-substituted R groups.

Illustrative of such organic pyrophosphates are tetraethyl pyrophosphate, tetramethyl pyrophosphate, dimethyl diethyl pyrophosphate and bis(2,4-dichlorophenyl) diethyl pyrophosphate. Where pyrophosphates are employed, as many as 15, but more preferably 12 moles of sulfur trioxide donor may be complexed with each mole of phosphorous compound.

Other Lewis bases suitable as complexing agents are those Lewis bases which contain oxygen or nitrogen.

The nitrogen containing Lewis bases which form active complexes with sulfur trioxide donors and which are suitable for sulfonation of the unsaturated polymers of this invention have the general formulae:
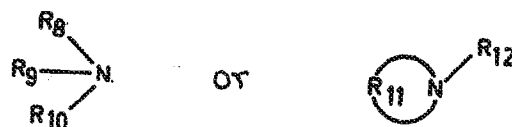
wherein R_8, R_9, R_{10} and R_{12} are each independently hydrogen, or C_1 to C_{36} alkyl, aryl, alkaryl or aralkyl, with the proviso that where R_8 and R_9 are hydrogen, R_{10} must not be hydrogen and R_{11} is selected from the group consisting of C_3 to C_{36} alkylene. Broadly speaking, the nitrogen containing Lewis base may be any primary, secondary or tertiary organic amine or a cyclic organic amine. Where the R_8, R_9, R_{10}, R_{11} or R_{12} radicals contain more than two carbon atoms, they may be heterogeneous organic radicals containing oxygen, chlorine, nitro groups or mixtures thereof. That is, R_8, R_9, R_{10}, R_{11} and R_{12} may be ethereal, or be substituted by halogen atoms, nitro groups or comprise both ethereal and substituted groups. With reference to R_8, R_9, R_{10}, R_{11} and R_{12} of these formulae, the term "substituted analogues" as used in the specification means groups as described and substituted with the substituents referred to above. For the purposes of this invention, where R_8, R_9, R_{10}, R_{11} and R_{12} are ethereal, they shall be considered to fall in the class of "substituted analogues". In cases where R_8, R_9, and R_{10} contain aryl, alkaryl or aralkyl groups, the use of excess sulfur trioxide donor is required to compensate for any sulfonation of the aromatic units.

Illustrative of these nitrogen containing Lewis bases are trimethylamine, triethylamine, dimethylaniline, diethylaniline, piperidine, morpholine, N-ethyl morpholine, diethylaminoacetal, and tri 2-chloroethylamine.

Other suitable complexing agents containing nitrogen may be represented by the formula:
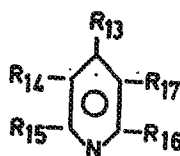
wherein R_{17}, R_{16}, R_{13}, R_{14} and R_{15} are hydrogen, halogen, or C_1 to C_{46} alkyl, aryl, alkaryl or aralkyl. In cases where R_{17}, R_{16}, R_{13}, R_{14} and R_{15} contain aromatic units, the use of excess sulfur trioxide donor is required to compensate for any sulfonation of these units. The organic R_{17}, R_{16}, R_{13}, R_{14} or R_{15} radicals may contain halogen or oxygen atoms, or nitro groups. With reference to these R_{13} to R_{17} groups, the term "substituted analogues" as used in the specification means groups as described and substituted with oxygen or halogen or containing oxygen in the carbon chain. In addition, fused cyclic ring and polymeric structures are satisfactory.

Illustrative of this type of compound are pyridine, 2-methyl pyridine, 2,6-dimethyl pyridine, quinoline, quinaldine, and poly-2-vinyl pyridine.

The preferred nitrogen containing complexing agents are triethylamine and tri-n-propylamine. The molar ratio of sulfur trioxide donor to nitrogen in the complex may be as high as 5 to 1, but the preferred ratio is 1 to 1.

Suitable solvents for the preparation of these complexes are chlorinated hydrocarbons. The preferred concentration of complex in solution is from 5 to 20% by weight, more preferably, 10 to 15%. The complexes may also be prepared by direct addition of the reagents if precautions are taken to dissipate the heat evolved. The reactions of complexes of SO_3 with molecules containing nitrogen and the polymer backbones containing aromatic nuclei have been found to be nonquantitative. Therefore, the use of excess complex is desirable in such reactions.

Oxygen containing Lewis bases have been found useful for complexing sulfur trioxide donor to facilitate reaction with the unsaturation of polymer molecules. The general formulae of such bases are:

$$R_{18} \diagdown \!\!\!\!\!\! {}_{O} \quad \text{or} \quad R_{20} \, O$$
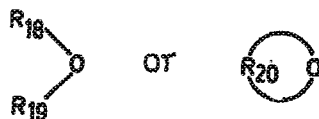
wherein R_{18} and R_{19} are each independently C_2—C_{36} alkyl, aryl, alkaryl or aralkyl and R_{20} is C_3—C_{36} alkylene; R_{20} may be a substituted alkylene; the substituents may be C_1 to C_{20} alkyl, aryl, alkaryl or aralkyl. For R_{18}, R_{19} or R_{20} greater than C_{20} halogen, nitro groups and ethereal oxygen atoms may also be present. With reference to R_{18}, R_{19} and R_{20}, the term "substituted analogues" as used in the specification means R_{18}, R_{19} and R_{20} substituted as described above. Also suitable as oxygen containing Lewis bases are dioxane and substituted dioxanes. The presence of aryl, alkaryl or aralkyl groups in the base demands the use of excess SO_3 since some of the SO_3 is used in sulfonation of the aromatic groups.

Illustrative of the oxygen containing Lewis bases suitable for use in the practice of this invention are tetrahydrofuran, para-dioxane, 2,3-dichloro-1,4-dioxane, meta-dioxane, 2,4-dimethyl-1-1,3-dioxane, 2 phenyl-1,3-dioxane and bis(2-dichlorethyl) ether.

Other oxygen containing Lewis bases suitable as complexing agents are esters having the general formula:

$$\overset{O}{\underset{\|}{R_{21}-C-O-R_{22}}}$$
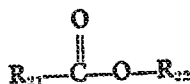
wherein R_{21} and R_{22} are C_1 to C_{10} alkyl, phenyl or benzyl or their nitro- or halo-substituents. Illustrative of such esters are benzyl acetate, butyl acetate, butyl propionate, methyl benzoate, hexyl acetate, isobutyl benzoate, ethyl-o-bromobenzoate, p-nitrophenyl acetate, ethyl-n-butyrate, ethyl stearate and ethyl phenyl acetate.

The molar ratio of SO_3 donor to base may be as high as 15 to 1; preferably about 9:1 to about 1:1, more preferably about 5:1 to about 1:1, most preferably about 2:1 to about 4:1, e.g. 3:1.

The preferred solvents for preparation of the complexes of sulfur trioxide donor with complexing agents containing oxygen are chlorinated hydrocarbons or the oxygen containing complexing agent. Illustrative of such chlorinated solvents are carbon tetrachloride, dichloroethane, chloroform and methylene chloride. The complexes may also be prepared by direct addition of reagents if precautions are taken to dissipate evolved heat.

The reactions of ethereal complexes of SO_3 with the polymer chains containing aromatic groups has been found to be nonquantitative. Therefore, the use of excess complex is desirable to give the required amount of sulfonation.

Any of the phosphorus, oxygen or nitrogen containing Lewis bases may be used individually as complexing agents or mixtures thereof may be used. The preferred complexing agents are the organic phosphorous compounds.

Where the phosphorus containing complexing agent is used, the complex may contain 1 to 15 moles of sulfur trioxide donor per mole of complexing agent, preferably 1 to 9 moles, more preferably 1 to 5 moles, most preferably 2 to 4 moles, e.g. 3 moles.

The preferred complexing agents are trimethyl phosphite, triethyl phosphite and triethyl phosphate, more preferably triethyl phosphate. The preferred sulfur trioxide donor is SO₃.

In the practice of this invention, the polymer to be sulfonated is dissolved in a suitable solvent and reacted with a complex comprising the complexing agent and the sulfur trioxide donor at a temperature between —100° C and 100° C. The solvent medium must be a mutual one for the polymer and the complex. The solvent is preferably non-aromatic.

Illustrative of such solvents are alkanes, chlorinated alkanes, ethers, esters, or mixtures thereof. The alkane may be linear, branched or cyclic.

Illustrative of these alkanes are hexane, pentane, butane, cyclohexane, heptane and homologues thereof and analogues thereof. Illustrative of the chlorinated alkanes are methyl chloride, ethyl chloride, dichloroethane, chloroform, methylene chloride, carbon tetrachloride or any higher alkane or chlorinated alkane.

Illustrative of the suitable ethers and esters are tetrahydrofuran, p-dioxane, diethyl ether, amyl ethyl ether, bis-pentachloroethyl ether, bis-β-chloroisopropyl ether, butyl acetate, isoamyl acetate and cyclohexylacetate.
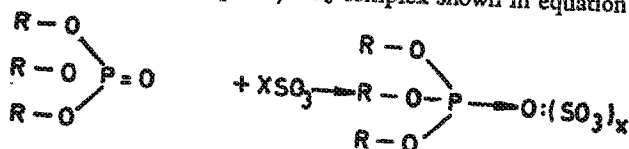
Preferably, the solids content of the polymer solution is less than 25 wt. %. More preferably, 5 to 20 wt. %, most preferably 10 to 20 wt. %. Though cements having solid contents as high as 60 wt. % may be used there is a handling problem due to the high viscosity.

The complex may be formed at —100° C. to +100° C., more preferably —40 to +40° C. Preferably, the complex is prepared immediately prior to use. In situ preparation of the complex in the polymer solution has also been found to be adequate. Where the complex is prepared prior to use, its concentration in solvent should be 0.5 to 25 wt. %, more preferably 1 to 20 wt. %, most preferably 10 to 20 wt. %, e.g. 18 wt. %.

Sulfonation of the polymer is conducted at a temperature between —100 and +100° C. Sulfonation occurs when the complex in solution is added to the polymer solution. The reaction time may be from 5 seconds to 3 hours. The product remains soluble throughout the reaction period. The product is best recovered by flashing off the solvents in hot water. The water also decomposes the unreacted complex.
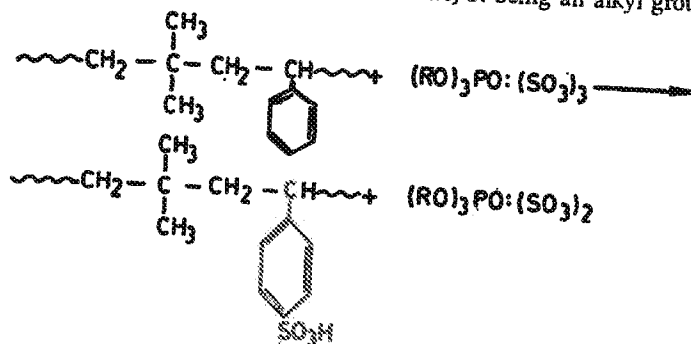
The sulfonated polymers may be purified further by kneading in the presence of low boiling ketones or alcohols. The preferred materials for this purpose are acetone and methanol. After kneading, the polymers are dried on a hot mill. The recovered products are soluble in a variety of solvents, which indicates that the sulfonation has been accomplished without crosslinking.

Illustrative of the sulfur trioxide complex formed by reacting a complexing agent with SO₃ is the trialkyl phosphate/SO₃ complex shown in equation (1):

$$\begin{array}{c} R-O \\ R-O \\ R-O \end{array} P=O \;+\; XSO_3 \longrightarrow \begin{array}{c} R-O \\ R-O \\ R-O \end{array} P\!-\!\!-\!\!O\!:\!(SO_3)_x$$

wherein R is an alkyl group and X represents the moles of SO₃ per mole of phosphorus compound. Preferably, X is about 1 to about 7; more preferably, about 2 to about 4, e.g. 3.

A typical sulfonation reaction proceeds as follows, R being an alkyl group:

$$\sim\sim CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - CH\sim\sim \;+\; (RO)_3PO\!:\!(SO_3)_3 \longrightarrow$$

$$\sim\sim CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - CH\sim\sim \;+\; (RO)_3PO\!:\!(SO_3)_2$$
$$SO_3H$$

The metal ions which are suitable in forming the ionic copolymers of the present invention may be classified into two groups; non-complexed metal ions and complexed metal ions. In the non-complexed metal ion, the valence of the ion corresponds to the valence of the metal. These metal ions are obtained from commonly known and used metal salts.

The complex metal ions are those in which the metal is bonded to more than one type of salt group and at least one of which is ionized and one of which is not. Since the formation of ionic polymers requires only one ionized valence, such complex metal ions are equally well suited for use in the present invention. The utility of complex metal ions employed in the formation of ionic copolymers corresponds in their ionized valences to those of the non-complexed ions. The monovalent metals are, of course, excluded, but the higher valent metals may be included depending upon how many metal ions are complexed and how many can be ionized. The preferred complex metal ions are those in which all but one of the metal valences are complexed and one is readily ionized. In particular, the mixed salts of very weak acids such as stearic acid and ionized acids such as formic and acetic acids may be utilized.

The non-complexed metal ions which are suitable in forming ionic copolymers in the present invention comprise mono, di, tri and tetravalent metals in the Groups I, II, III, IV, V, VIB, VIIB and VIII of the Periodic Table of the Elements. (See page B—3, Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., 47th Ed.) Suitable monovalent metal ions are Na^+, K^+, Li^+, Cs^+, Ag^+, Hg^+, and Cu^+. Suitable divalent metal ions are Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Cu^{+2}, Cd^{+2}, Hg^{+2}, Sn^{+2}, Fe^{+2}, Pb^{+2}, Co^{+2}, Ni^{+2}, and Zn^{+2}. Suitable trivalent metal ions are Al^{+3}, Sc^{+3}, Fe^{+3}, and Y^{+3}. Suitable tetravalent metal ions are Sn^{+4}, Zr^{+4}, Ti^{+4}, and Pb^{+4}.

In addition to the metal ions, other basic materials such as primary, secondary and tertiary amines may be to form the ionic bonds. The preferred amines have a basicity constant, K_b, greater than 10^{-3}. The basicity constant may be defined by the expression:

$$K_b = \frac{[Product]}{[\sim SO_3H]\,[Amine]}$$

for the reaction $\sim SO_3H + Amine \longrightarrow Product$
where:

[Product] = Concentration of Product
[$\sim SO_3H$] = Concentration of Sulfonic Acid groups in the polymer
[Amine] = Concentration of amine

The preferred amines have a K_b value in the range of 10^{-3} to about 10^{+6}, preferably about 10^3 to 10^{-2}. Illustrative of such amines are anhydrous piperazine, tri-n-propylamine, triethylamine and triethanolamine. The secondary and tertiary amines are most preferred, especially piperazine and tri-n-propylamine.

The melt fabricability of the ionic polymer is affected not only by the number of crosslinks but to a much larger extent by the nature of the crosslink. For example, in the preparation of sulfonic acid ionomers of homogeneous styrene-isobutylene copolymers, the ionic content, where a monovalent salt [M^+] is used is preferably 1 to 20 moles of [M^+ styrene sulfonate] groups per 100 monomer units in the polymer; more preferably, 4 to 16 moles; most preferably 8 to 12 mole.

In a sulfonation process in accordance with this invention, the SO_3-complex is present in the reaction medium at 0.2 mole to 21 moles per 100 repeating units in the polymer; preferably 1 to 20 moles; more preferably 2 to 16 moles; most preferably 4 to 12 moles. The sulfonated elastomers of this invention contain 0.2 mole % to 21 mole % $\sim SO_3H$ in the elastomer; more preferably 2 to 16 mole %; most preferably 4 to 12 mole %. From 1 to 100% (numerically) of the $\sim SO_3H$ groups may be neutralized to form the ionomer.

Throughout the specification and claims the term " mole % sulfonic acid groups " means moles sulfonic acid groups per 100 monomer (i.e. repeating) units.

For divalent metal ions [M^{+2}] such as Zn^{+2}, Ca^{+2}, Cu^{+2}, and Ba^{+2}, the ionic content is preferably less than 12 moles of [M^{+2} (styrene sulfonate)$_2$] groups per 100 monomer units. For trivalent metal ions [M^{+3}] such as Al^{+3}, Fe^{+3}, and Co^{+3}, the

ionic content should preferably be less than 1.0 mole of [M^{+3} (styrene sulfonate)$_3$] groups per 100 monomer units.

The distinct advantages of the sulfonated elastomers, and corresponding ionomers, of this invention may be more readily appreciated by reference to the following examples, of which Example 1 is a comparative example.

EXAMPLE 1

A homogeneous styrene-isobutylene copolymer was prepared in a conventional overflow reactor. The reactor contained a central chamber housing a stirrer and two outer chambers for circulation of reactants. The reactor was suspended in a temperature bath. Two feed lines were used. The first contained the monomers dissolved in a solvent and the second contained dissolved catalyst. Both feeds were pre-chilled to the proper temperature.

The reaction temperature was −90° C. and the reaction time was 30 minutes. The monomer feed comprised 40 weight % styrene and 60 weight % isobutylene. The monomers were diluted to a 17.5 % concentration in a 60/40 (by vol.) mixture of methyl chloride and hexane. The catalyst was AlCl$_3$ at 0.12 wt. % concentration.

After a reaction time of 30 minutes, the catalyst activity was destroyed by quenching in isopropyl alcohol. The copolymer was recovered and dried. The intrinsic viscosity was 1.099 (1 g./liter of toluene at 25.84° C.). The copolymer had a viscosity average molecular weight of 330,000; a styrene content of 39.3 weight % was determined by nuclear magnetic resonance spectroscopy.

The product displayed poor stress bearing capacity, as shown in Table I, and was soluble in certain non-polar solvents such as benzene and carbon tetrachloride but did not swell in polar solvents such as alcohol or water as evidenced in Table II.

EXAMPLE 2

The product of Example 1 was sulfonated by the method disclosed in U.S. patent 3,072,618. Twenty grams of polymer was dissolved in 760 ml. of dry dichloroethane to which was added a 100 ml. solution of 3.35 ml. triethyl phosphate with 2.48 ml. of freshly distilled sulfur trioxide in dichloroethane. The reaction time was 10 minutes at 10° C. The polymer contained 7.12×10^{-4} equivalents of SO$_3$H per gram (i.e. 4.9 moles of sulfonated styrene per 100 monomer units in the copolymer).

The physical properties of the copolymer are shown in Table I and its solubility characteristics in Table II.

EXAMPLE 3

The product of Example 2 was converted into an ionic interpolymer by milling into it exact equivalents of sodium methoxide. On heating methyl alcohol is driven off. The material is easily processable, moldable, and re-workable. The strength properties are good (Table I). The material displays solvency properties similar to those of the product described in Example 2 (see Table II).

EXAMPLE 4

The material of Example 1 was sulfonated (using the general procedures outlined in Example 2) to obtain a product with 1.93×10^{-3} equivalents of SO$_3$H/gm. of polymer, as determined by titration (see Example 2) and elemental sulfur analyses. This corresponds to 13.3 moles of sulfonated styrene units per 100 monomer units. The material exhibits excellent stress supporting properties (see Table I) and a broad temperature range over which it is rubbery. It is easily re-processable under molding conditions (280° F. and 12 tons pressure). The material has increased resistance to non-polar solvents and decreased resistance to polar solvents (Table II).

EXAMPLE 5

The material of Example 1 was sulfonated by the method of Example 2 to obtain a product with 18.1 moles of sulfonated styrene units per 100 monomer units. The product was very strong and elastic (Table I) and re-processable under molding conditions. It was somewhat resistant to non-polar solvents but was greatly affected by polar solvents (see Table II).

EXAMPLE 6

The product of Example 5 was converted into an ionic interpolymer by milling in exact equivalents of sodium methoxide. The product was difficultly processable. Apparently, an upper limit for ionic character was barely exceeded.

EXAMPLE 7

The material of Example 5 was converted into an ionic interpolymer by the addition of ZnO such that 5 moles of sulfonated styrene/100 monomer units were made ionic. The product was easily processable and re-processable at molding temperature (280° F.) and pressure (12 tons). The product was quite strong (Table I) and had good non-polar solvent resistance (Table II).

EXAMPLE 8

The material of Example 1 was sulfonated by the method of Example 2 to obtain a product with 20.7 moles of sulfonated styrene units per 100 monomer units. The product was strong (Table I) and re-processable. The material was swollen somewhat by non-polar solvents and was greatly affected by polar solvents (Table II).

EXAMPLE 9

The material of Example 8 was converted into an ionic interpolymer by adding ZnO such that 10 moles of sulfonated styrene/100 monomer units were made ionic. The product was easily processable and reprocessable under molding conditions. The material was only slightly swollen by non-polar solvents. (Table II).

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TABLE I

Strength Properties of Sulfonated, Homogeneous Styrene-Isobutylene Copolymers at 25°C.
(Pull rate = 5"/min.)

Material* (Example)	Tensile Strength lb./in.^{2}	Modulus (300%) lb./in.^{2}	Elongation %
1. Styrene-Isobutylene Copolymer	275	50	1900
2. 4.9 mole % ~ SO$_3$H	850	179	1100
3. 4.9 mole % ~ SO$_3$⁻Na⁺	750	390	750
4. 13.3 mole % ~ SO$_3$H	1470	663	500
5. 18.1 mole % ~ SO$_3$H	1350	467	580
7. 13.1 mole % ~ SO$_3$H + 5 mole % Zn (~ SO$_3$⁻)$_2$	1000	420	510
8 20.7 mole % ~ SO$_3$H	930	463	440
9. 10.7 mole % ~ SO$_3$H + 10 mole % Zn (~ SO$_3$⁻)$_2$	1440	1100	380

* Unfilled.

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TABLE II

Behaviour of Sulfonated Homogeneous Styrene-Isobutylene
Copolymers Toward Polar and Non-Polar Solvents (At 25°C.)

Material (Example)	Volume Swell %			
	Benzene	Carbon Tetrachloride	Methanol	Watder
1. Styrene-Isobutylene Copolymer	soluble	soluble	0	0
2. 4.9 mole % ~SO$_3$H	soluble	soluble	226	17.3
3. 4.9 mole % ~SO$_3^-$Na$^+$	soluble	923	4.2	3.3
4. 13.3 mole % ~SO$_3$H	170	307	soluble	97.4
5. 18.1 mole % ~SO$_3$H	13.9	50.8	soluble	191.6
7. 13.1 mole % ~SO$_3$H$^+$ 5 mole % Zn (~SO$_3^-$)$_2$	22.0	62.1	soluble	170
8. 20.7 mole % ~SO$_3$H	17.6	48.6	soluble	150.5
9. 10.7 mole % ~SO$_3$H ±10.0 mole % Zn (~SO$_3^-$)$_2$	29.6	89.9	soluble	58.9

EXAMPLE 10

Using the method of Example 2, styrene-isobutylene copolymer was sulfonated at various levels. The modulus was determined on sulfonated samples both before and after preparation of ionomers by the method of Example 3.

Referring to the two figures of the accompanying drawings, Fig. 1 shows the effect of hydrogen bonding and ionic bonds on modulus. The figure shows that as the mole % of SO_3H groups increases, there is a slight increase in modulus.

By contrast, conversion of the product to ionomers radically increases the modulus. For example, the Figure shows a sample of styrene-isobutylene copolymer containing about 16.15 mole % SO_3H converted to an ionomer with varying degrees of ionic crosslinking. Surprisingly, there is a radical change in modulus with ionic content.

Fig. 2 shows the temperature dependence of tensile strength of unsulfonated styrene-isobutylene copolymer as compared with the same product containing 16.15 mole % SO_3H and varying degrees of ionic content.

Curve A shows the tensile strength of the unsulfonated copolymer as a function of temperature. At 20° C. the copolymer has a tensile strength of less than 375 lb./in.^{2}. At less than 60° C., the tensile strength is virtually zero (0).

By contrast, copolymer containing about 16.15 mole % SO_3H (Curve B) has a tensile strength at 20° C. in excess of 600 psi and nearly 500 psi at 100° C.

Conversion of only about 4 mole % SO_3H to the calcium ionomer (Curve C) results in a product having a tensile strength in excess of 900 psi at 20° C. and about 550 psi at 100° C.

The advantages of using a monovalent ion to form the ionomer are shown in Curve D. With about 12 mole % of the SO_3H groups converted to the sodium salt, the copolymer has a tensile strength about 1500 psi; however, at 100° C. the tensile strength is less than 400 psi. Hence, despite a high room temperature tensile strength, the copolymer is readily processed at moderate temperatures.

It is evident from the foregoing examples that useful styrene-isobutylene elastomers may contain 4.9 to 20.7 mole % SO_3H groups. As little as 1 mole % $(SO_3)_nM$ wherein n represents the valence of the metal ion, M, results in an ionomer of improved properties. More preferably, the ionic content, i.e. $(SO_3)_nM$ groups, is 2 to 18 mole %; most preferably 4 to 12 mole %.

EXAMPLE 11

Previously examples described the sulfonation of a purified homogeneous styrene-isobutylene copolymer. It is not necessary to purify the product before sulfonation, as described in this example. The material of Example 1 was prepared again, except that the catalyst activity was not killed by quenching the reaction in isopropyl alcohol. Rather, the reaction liquor (methyl chloride/hexane=60/40 by vol.) was maintained at —40° C. and the styrene-isobutylene copolymer was sulfonated directly with the triethyl phosphate and sulfur trioxide reagents. The polymer was recovered and analyzed. The material contained 5.57 moles of sulfonated styrene/100 monomer units. The properties of the material were found to be identical in all respects to a carefully purified preparation (in dichloroethane).

It is readily evident that the ionic polymer of homogeneous styrene-isobutylene copolymer is a superior thermoplastic material suitable for use in fabrication by extrusion, injection molding, or compression molding. Because of its unusual behaviour toward solvents, the product finds utility in the fabrication of rubberized paints, alcoholic thickeners, flocculents, dye receptors and adherents to metals.

EXAMPLE 12

A styrene-chlorobutyl graft polymer was prepared using the method of British Patent 1,174,323. Specifically, 100 grams of chlorobutyl rubber HT-1066 was dissolved in a solvent system of 900 ml. of heptane and 1000 ml. propane at —50° C. 206.3 gm. of freshly distilled styrene was added and then 2.87 gm. of $AlEt_2Cl$ catalyst. The reaction proceeded for 90 minutes. At the end of this time the product was recovered and dried; the yield was 249.0 gm. The product was extracted with acetone to remove styrene homopolymer. The rest of the material was solubilized in MEK (methyl ethyl ketone) to separate the gelatinous precipitate. The MEK soluble fraction was recovered and dried. 5 gm. of this material was dissolved in 190 ml. of dichloroethane. The sulfonation procedure of U.S. Patent 3,072,618 was used then. 0.38 ml. of triethyl phosphate was added followed by 0.28 ml. of sulfur trioxide at 5° C. The reaction proceeded for 10 minutes and was terminated by quenching, and the product recovered.

Analysis of the styrene-butyl graft copolymer showed an intrinsic viscosity of 0.77 in toluene and 42% styrene by infrared spectroscopy. The properties of a compression molded pad were: tensile strength=2800 lb./in.²; elongation at break= 375%.

Acid base titration of the ionic styrene-butyl graft copolymer in a 50/50 mixture of toluene and methanol with 0.1 N-standard KOC(CH₃)₃ showed that this product had 8.83×10^{-4} acid equivalents per gram. The sulfur content was found to be 2.84% by weight. The product thus contained 6.5 mole % sulfonic acid groups.

The sulfonated styrene-butyl graft copolymer was made into the ionic product by dissolving the material in a 50/50 mixture of toluene and methanol and adding 8.83×10^{-4} equivalents of sodium methoxide. The precipitated product was dried and compression molded at 300° F. and 12 tons of pressure for 10 minutes. The molded object was *thermoplastic* and could be remolded under the previous conditions. The properties of a molded pad were tensile strength=1370 lb./in.² and elongation at break —225%. The ionic graft copolymer was decidedly stiffer than the non-ionic graft copolymer.

The ionic graft copolymer displayed unusual solvent resistance compared to the non-ionic graft copolymer. A summary of the effects of various solvents is shown in Table III. It is seen that while the non-ionic graft copolymer was highly swollen or dissolved in certain organics, the ionic graft copolymer was insoluble or was merely swollen.

TABLE III

Behaviour of Graft Copolymer and Ionic Graft
Copolymer Toward Solvents

Solvent	Graft Copolymer	Ionic Graft Copolymer
Benzene	soluble	swells slightly
Carbon tetrachloride	soluble	swells
Heptane	highly swollen	insoluble (not swollen)
Methanol	insoluble	insoluble
Acetone	insoluble	insoluble
Methyl Ethyl Ketone	soluble	insoluble
Water	insoluble	insoluble

EXAMPLE 13

A commercial styrene butadiene rubber containing 23 wt. % styrene and 77 wt. % butadiene having a membrane osmometry number average molecular weight of 120,000 was sulfonated in the following manner.

The SBR was purified by dissolving 50 grams of rubber in 500 ml. of hexane and precipitating the polymer in 10 liters of methanol. The rubber was dried on a rubber mill at about 240° F.

Five gram quantities of the purified material were sulfonated using an (EtO)₃PO:(SO₃)₂ complex to form polymers having various levels of sulfonation. Sulfonation was carried out in solvent mixtures of cyclohexane and methylene chloride. The polymer was dissolved in the solvent mixture and the complexes which were prepared in methylene chloride was added dropwise with stirring. The reaction was carried out over a ten (10) minute period at 25° C.

Conversion of the sulfonic acid containing polymers to ionomers was accomplished by reacting the sulfonic acid polymer with twice the stoichiometric quantity of NaOH dissolved in methanol. The polymers were recovered by dropping the polymer solution into boiling water, thereby flashing off the solvents and precipitating the polymer. The recovered polymer was dried at 130° C.

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Table V summarizes the various experimental results. It is noted that the sulfonic acid polymer is soluble at 6.5 mole percent SO_3H which indicates there has been no crosslinking. The polymers were thermoplastic and could be molded and remolded at 130° C. and 9000 psig.

Although sulfonation has been described in terms of sulfonation of the aromatic nucleus, it is thought that in polymers such as SBR which contain a high degree of non-aromatic unsaturation, the sites of unsaturation are also sulfonated. Not wishing to be bound by the theory, it is postulated that sulfonic acid moieties are distributed between sites of non-aromatic unsaturation and aromatic rings dependent on the mole ratio of the unsaturation to aromatic ring and the reactivity of the sites sulfonated. It is thought that the sites of unsaturation are more reactive than the aromatic ring. Hence, in a polymer such as SBR the preponderance of the sulfonic acid groups are added at non-aromatic unsaturation sites.

Since the SO_3H groups may be pendant either from the aromatic ring or the polymer backbone, their concentration in the polymer is expressed in mole % based on the polymer rather than the aromatic units. It is desirable that the sulfonated SBR of this invention contains 0.2 to about 20 mole % SO_3H groups; preferably about 1 to about 20 mole %; more preferably about 0.5 to about 12 mole %, suitably 0.48 to 6.5 mole %, most preferably about 1 to about 8 mole %, e.g., 3.0 mole %. From about 1 to 100 % of the SO_3H groups may be neutralized to form the ionomer.

TABLE V

Preparation and Properties of a Sulfonated Styrene-Butadiene Copolymer (SBR)

gm. SBR	ml. Solvents	Moles Reactivity Available in Solution	Moles SO₃ Used	Moles (EtO)₃PO Used	ml. CH₂Cl₂	gm. NaOH	ml. CH₃OH	Mole % SO₃H	Mole % SO₃Na	Condition of Reaction
5	100 ml. cyclohexane + 40 ml. CH₂Cl₂	0.0823	4.1×10^{-4}	1.37×10^{-4}	1.0	0	0	0.48	0	soluble
5	100 ml. cyclohexane + 40 ml. CH₂Cl₂	0.0823	4.1×10^{-4}	1.37×10^{-4}	1.0	0.0328	1.0	0	0.50	soluble
5	100 ml. cyclohexane + 40 ml. CH₂Cl₂	0.0823	1.23×10^{-3}	4.1×10^{-4}	1.0	0	0	1.42	0	soluble
5	100 ml. cyclohexane + 40 ml. CH₂Cl₂	0.0823	1.23×10^{-3}	4.1×10^{-4}	1.0	0.0984	1.0	0	1.51	soluble
5	100 ml. cyclohexane + 40 ml. CH₂Cl₂	0.0823	2.46×10^{-3}	8.2×10^{-4}	2.0	0	0	2.82	0	soluble
5	100 ml. cyclohexane + 40 ml. CH₂Cl₂	0.0823	2.46×10^{-3}	8.2×10^{-4}	2.0	0.1968	2.0	0	2.90	soluble
5	100 ml. cyclohexane + 40 ml. CH₂Cl₂	0.0823	5.76×10^{-3}	1.92×10^{-3}	3.0	0	0	6.5	0	soluble

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The improvement in physical properties is readily demonstrated by comparing styrene-butadiene copolymer with the same polymer both sulfonated and converted to the sodium ionomer. Physical properties are shown in Table VI.

TABLE VI

Properties of Sulphonated SBR

Mole % SO_3H	Mole % SO_3Na	Tensile lb/in²	Modulus (50%) lb/in²	Modulus (30%) lb/in²	% Elong.	% Set at Break
0	0	35	39	41	570	400
0.48	0					
0.48	0	75	40	63	680	350
0	0.5	64	40	53	800	350
1.42	0					
1.42	0	150	60	95	700	200
0	1.51	230	90	170	630	40
2.82	0	460	81	230	580	30
0	2.90	530	156	375	650	5
6.5	0	650	170	600	340	0

It is readily evident that sulfonation improves properties of the polymer. For example, with as little as 0.48 mole % SO_3H in the polymer, the tensile strength has been increased more than 100%. The sulfonated polymers may be cured in any conventional manner.

EXAMPLE 14

Using the method of U.S. Patent 3,265,765, a styrene-butadiene block polymer was prepared containing 30 wt. % styrene (S) and 70 wt. % butadiene (B). The structure of the polymer was S—B—S wherein S represents styrene sequences having a number average molecular weight of about 15,000 and B represents butadiene sequences having number average molecular weights of about 50,000.

The polymer was sulfonated in the manner of Example 14. The results are tabulated in Table VII.

TABLE VII

Sulfonation of a Styrene-Butadiene-Styrene Block Copolymer

gm. Polymer	Moles Reactivity Available in Solution	Solvent System	Moles SO_3 Used	Moles $(EtO)_3PO$ Used	Ml. $ClCH_2CH_2Cl$	Mole % SO_3H
10	0.158	100 ml. cyclohexane + 40 ml. CH_2Cl_2	1.59×10^{-3}	1.59×10^{-3}	2.0	0.45
10	0.158	100 ml. cyclohexane + 40 ml. CH_2Cl_2	6.34×10^{-3}	6.34×10^{-3}	5.0	0.81
10	0.158	100 ml. cyclohexane + 40 ml. CH_2Cl_2	1.27×10^{-2}	1.27×10^{-2}	10.0	1.24

EXAMPLE 15

The styrene-isobutylene copolymers prepared in the manner of Example 1 were sulfonated using complexing agents other than the phosphorous containing Lewis bases. Table VIII shows the results of sulfonation using p-dioxane, triethylamine and tetrahydrofuran as the complexing agent. It is readily evident that these Lewis bases are effective complexing agents.

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TABLE VIII

Sulfonation of Styrene-Isobutylene Copolymers

Complex Preparation

Polymer Styrene Content (mole %)	gm	ml. Solv. (Carbon Tetrachloride)	Moles SO_3	Moles Complexing Agent	Ml. Solvent	% Sulfur in Product	Mole % SO_3H
18.8 ($\overline{Mn}$ = 175,000)	10	200	0.0144	0.0144 p-dioxane	10 CH_2Cl_2	2.84	5.28
18.8 ($\overline{Mn}$ = 175,000)	10	200	0.0144	0.0144 $(Et)_3N$	15 CH_2Cl_2	0.29	0.54
50.0 ($\overline{Mm}$ = 110,000)	10	200	0.0313	0.0313 THF	20 CH_2Cl_2	0.26	0.66
50.0 ($\overline{Mn}$ = 110,000)	10	200	0.0313	0.0313 $(Et)_3N$	20 CH_2Cl_2	0.15	0.38

All of the products formed were soluble in the reaction medium. The products were found to have improved physical properties even without formation of the ionomer. For example, sulfonated polymer containing 1.24 mole % SO_3H was more resistant to flow in a cold press. The improved physical properties were attributed to hydrogen bonding. The product may be readily converted to the ionomer by the method of Example 14.

WHAT WE CLAIM IS:—

1. A sulfonated elastomer containing monocyclic aromatic groups and 0.2 to 21 mole % sulfonic acid groups as herein defined.

2. A sulfonated elastomer as claimed in claim 1, containing 0.2 to 16 mole % sulfonic acid groups.

3. A sulfonated elastomer as claimed in claim 2, containing 0.2 to 12 mole % sulfonic acid groups.

4. A vulcanizable sulfonated elastomer containing monocyclic aromatic groups and having a sulfonic acid group content as claimed in any preceding claim.

5. A vulcanizable sulfonated elastomer comprising a styrene-butadiene copolymer having a sulfonic acid group content as claimed in any of claims 1 to 3.

6. A vulcanizable sulfonated elastomer as claimed in claim 5, containing 0.48 to 6.5 mole % sulfonic acid groups.

7. A vulcanizable sulfonated elastomer comprising a styrene-butyl rubber graft polymer having a sulfonic acid group content as claimed in any of claims 1 to 3.

8. A vulcanizable sulfonated elastomer comprising a graft polymer of a styrene-acrylonitrile copolymer on polybutadiene, the graft polymer having a sulfonic acid group content as claimed in any of claims 1 to 3.

9. A vulcanizable sulfonated elastomer comprising a graft polymer of styrene on polybutadiene, the graft polymer having a sulfonic acid group content as claimed in any of claims 1 to 3.

10. A sulfonated homogeneous styrene-isobutylene copolymer (as herein defined) having a sulfonic acid group content as claimed in any of claims 1 to 3.

11. A sulfonated elastomer as claimed in any preceding claim and substantially as herein described.

12. A sulfonated elastomer as claimed in any of claims 1 to 11 and substantially as herein described with reference to any one of Examples 2, 4, 5, 8 and 12 to 15.

13. A process for preparing a sulfonated elastomer claimed in any of claims 1 to 10, which comprises:

(a) dissolving the unsulfonated form of the elastomer in a solvent, which is also a solvent for the said complex of (b), and

(b) reacting the elastomer at a temperature between −100° C and 100° C with sufficient of an SO_3 complex, prepared by reacting a Lewis base containing nitrogen, phosphorus or oxygen and a sulfur trioxide donor, to introduce the required sulfonic acid group content into the elastomer.

14. An ionomer comprising a sulfonated elastomer as claimed in any of claims 1 to 10 in which at least 1% of the sulfonic acid groups have been neutralized to form the corresponding amine or metal salt, wherein the amine is a primary, secondary or tertiary amine and the metal is at least one selected from Groups I to V, VIB, VIIB and VIII of the Periodic Table of the Elements herein identified.

15. An ionomer as claimed in claim 14, wherein the metal is sodium, potassium, calcium, copper, zinc, nickel, barium, aluminium or mixtures thereof.

16. An ionomer as claimed in claim 14 or claim 15 and substantially as described herein.

17. An ionomer as claimed in claim 14 or claim 15 and substantially as described herein with reference to any one of Examples 3, 6, 7, 9, 12 and 13.

K. J. VERYARD,
15 Suffolk Street,
London, SW1Y 4HS.
Agent for the Applicants.

1,268,264 COMPLETE SPECIFICATION

2 SHEETS This drawing is a reproduction of
the Original on a reduced scale.
SHEET 1

FIG.1.

INFLUENCE OF HYDROGEN BONDS AND
IONIC BONDS ON THE MODULUS

FIG.2.

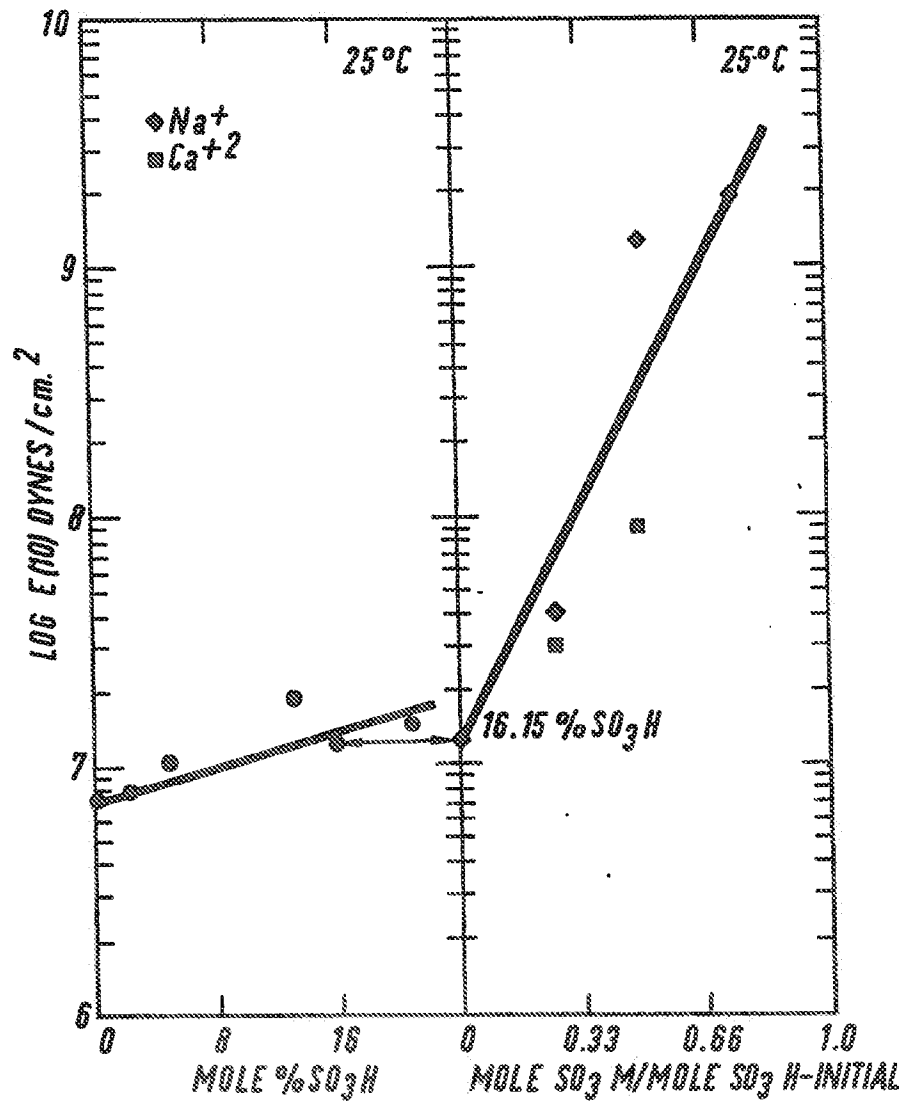## TEMPERATURE DEPENDENCE OF TENSILE STRENGTH FOR HYDROGEN BONDED AND IONIC INTERPOLYMERS